

# CEMENT AND LIME MANUFACTURE

PUBLISHED 20TH OF EACH MONTH.

PRICE 1/- A COPY.

ANNUAL SUBSCRIPTION 12/- POST FREE.

PUBLISHED BY  
CONCRETE PUBLICATIONS LIMITED  
14 DARTMOUTH STREET, LONDON S.W.1

TELEPHONE: WHITEHALL 4591  
TELEGRAPHIC ADDRESS:  
CONCRETIVUS PARL, LONDON

PUBLISHERS OF  
"CONCRETE & CONSTRUCTIONAL ENGINEERING"  
"CONCRETE BUILDING & CONCRETE PRODUCTS"  
"CEMENT & LIME MANUFACTURE"  
"THE CONCRETE YEAR BOOK"  
"CONCRETE SERIES" BOOKS, ETC.



VOLUME XI. NUMBER 8

AUGUST 1938

## Gas Analysis at Cement Works.

AN article in *Tonindustrie Zeitung* (1937, pp. 915-924), describes the use of the Orsat apparatus on a cement works and sets out in detail its method of use and the ways of avoiding the errors which may arise. All the estimations are carried out by absorption methods, since, as the author points out, combustible gases occur in flue gas only in small amounts and therefore an ignition pipette is rarely necessary. The solutions are prepared as follows.

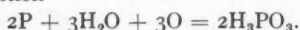
### Carbon Dioxide.

**POTASH SOLUTION.**—For the absorption of carbon dioxide a solution of caustic potash (not purified by alcohol) is used. One part by weight of potassium hydroxide is dissolved in two parts by weight of water. Every cubic centimetre of this solution will safely absorb 40 c.c. of carbon dioxide. The solution can also absorb other gases such as sulphur dioxide. The use of sodium hydroxide instead of potassium hydroxide is not recommended because it attacks glass more strongly and the sodium carbonate formed during absorption is difficult to dissolve. The solution can be used for a long time due to its great absorptive capacity. In general, the gas should be passed three times through the pipette for fresh solutions and four to five times for older solutions.

### Oxygen.

(a) **PHOSPHORUS SOLUTION.**—A reagent much used for absorbing oxygen is phosphorus in the form of thin sticks. It is kept in the pipette under water which acts as a protective liquid. The water is driven out of the pipette by the flue gas to be analysed, and the oxygen in it is absorbed by the wet phosphorus. The gas is allowed to stay in contact with the phosphorus for a length of time which depends upon the temperature; at ordinary room temperature about three

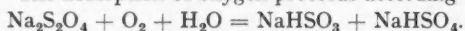
minutes is sufficient. The absorption of oxygen in the presence of water proceeds according to the equation



From this it can be seen that 1 g. of phosphorus will absorb 538 c.c. of oxygen. The product of the reaction is readily soluble in water. The absorption is complete when the cloudy vapour which is at first formed has almost completely disappeared. In the dark a glow can be seen during absorption which disappears when the reaction is complete. The best temperature for the reaction is 15 to 20 deg. C.—below this the absorption occurs more slowly and at 0 deg. C. it takes about an hour; above 40 deg. C. the absorption cannot be carried out because the phosphorus melts at this temperature. It is important to keep the phosphorus pipette in darkness otherwise a layer of red phosphorus is formed which hinders absorption. This can be avoided by using a pipette made of brown glass. The water which contains phosphorus and phosphorous acid should be renewed from time to time. Certain impurities can retard or completely prevent absorption. Such substances are sulphuretted hydrogen, sulphur dioxide, ethylene, acetylene, alcohol, petroleum, heavy hydrocarbons, and ammonia. If these substances are absent phosphorus is the most suitable absorption reagent for oxygen.

(b) PYROGALLOL SOLUTION.—Ten grammes of pyrogallol are dissolved in 30 c.c. of water, and 240 g. of caustic potash (not purified by alcohol) in 160 c.c. of water. In order to avoid oxidation the potash solution is poured into the pipette and then the pyrogallol solution is added, the mixing being carried out in the pipette itself. If the solution contains more pyrogallol than that recommended the mixture tends to froth, which makes estimation difficult. One cubic centimetre of solution can absorb 12 c.c. of oxygen. Solutions made with caustic soda absorb oxygen more slowly. It is, of course, necessary to remove the  $CO_2$  by means of caustic potash before absorbing oxygen.

(c) ALKALINE SODIUM HYPOSULPHITE SOLUTION.—Fifty grammes of sodium hyposulphite\* are dissolved in 250 c.c. of water and the solution mixed with 40 c.c. of caustic soda solution prepared by dissolving 500 g. of sodium hydroxide in 700 c.c. of water. The absorption of oxygen proceeds according to the reaction



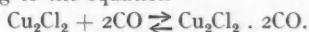
Sodium hyposulphite is converted to sodium bisulphite and sodium bisulphate. The solution is very active. One gramme of sodium hyposulphite can absorb 128 c.c. of oxygen. The advantage of this solution over phosphorus is that it works at comparatively low temperatures, and that substances which retard the action of phosphorus do not affect sodium hyposulphite.

#### Carbon Monoxide.

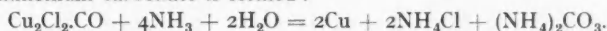
AMMONIACAL CUPROUS CHLORIDE SOLUTION.—Two hundred grammes of cuprous chloride are shaken with a solution consisting of 250 g. of ammonium chloride and 750 c.c. of water. Just before use, three parts by volume of this solution are mixed with one part by volume of ammonia solution (specific gravity

\* This is not the chemical usually known as "hypo" and used in photography. It is also known as sodium hydrosulphite.

0.910). The mixture should be filtered and a copper spiral suspended in it to prevent oxidation. The vapour pressure of the solution can be neglected. One cubic centimetre of this solution will absorb 16 c.c. of carbon monoxide, and the reaction proceeds according to the equation



This solution is not very active because the carbon monoxide is somewhat loosely held, so that with frequent use the gas tends to separate out again. Metallic copper is deposited slowly from used solutions, the carbon monoxide disappears, and ammonium carbonate is formed:



The concentration of CO in the mixture decreases slowly and the metallic copper which separates out protects the cuprous chloride from oxidation; eventually the cupric compounds are reduced to the cuprous state. It is best to work with two pipettes. First the gas is passed into a pipette containing fresh solution and then through one containing solution which has been used. The absorption of carbon monoxide proceeds slowly, and to speed up the reaction the gas should be passed repeatedly through the pipette. About ten to twelve times are suitable. When only small amounts of CO are present the estimation may be inaccurate. In order to find out if no CO is present a piece of palladium paper is placed in the tube leading to the pipette; this turns black in the presence of small quantities of CO. Besides CO the solution will also absorb acetylene, ethylene, carbon dioxide, and oxygen.

The solutions will last much longer if the exit tubes from the pipettes are connected to a common tube provided with a rubber balloon.

#### Water.

Water should be used for filling the measuring tube and the aspirator. Every liquid can absorb a certain amount of gas, the quantity depending on the type of gas, the liquid, the temperature, and the pressure. Increase of temperature reduces the absorptive capacity very rapidly. Ordinary tap water is more suitable than distilled water for the Orsat apparatus. Saturation of the protective liquid, e.g. with  $\text{CO}_2$ , is not necessary because it can in certain circumstances give up  $\text{CO}_2$  to the gas being analysed. It is much better to saturate it with the gas being analysed. In Table I are given the solubilities of a number of gases in water at 760 mm. pressure. The figures represent the number of parts by volume of gas soluble in one part by volume of water.

It can be seen from the table that water readily absorbs  $\text{CO}_2$ . In order to reduce this capacity for absorption a  $\frac{1}{4}$ -saturated solution of sodium chloride

TABLE I

Deg. C.	CO	$\text{CO}_2$	$\text{O}_2$	$\text{N}_2$
0	0.03537	1.713	0.04890	0.02348
5	0.03149	1.424	0.04286	0.02081
10	0.02816	1.194	0.03802	0.01857
15	0.02543	1.019	0.03415	0.01682
20	0.02319	0.878	0.03102	0.01542
25	0.02142	0.759	0.02831	0.01431

may be used, or water acidified with hydrochloric acid using methyl orange as indicator. In no case may the water be alkaline. It is usually of advantage to colour the water.

#### Care of Apparatus.

Before using the apparatus all taps and rubber tubes should be tested for leakage. It is very important to have the inside of the measuring cylinder quite clean, especially from oily matter, otherwise drops of water which adhere to the walls can cause considerable errors. The tubes can be cleaned best with a chromic acid-sulphuric acid mixture. The taps should be lubricated with a grease which does not saponify, otherwise they will stick fast. Paraffin or vaseline is suitable for this purpose.

#### The Gases.

In general, the gases are assumed to be perfectly dry and heat-balance calculations are carried out with the dry gas. Actually the gas which is analysed contains a large amount of water, most of which is deposited during sampling. If for any reason the gas contains more or less water than is necessary for saturation, the excess is deposited in the measuring cylinder or the deficiency is taken up if sufficient time is allowed. This results in a volume change. That the water content of the gas is important in carrying out an analysis can be seen from the following. One cubic metre of air saturated with water vapour contains

At 0 deg. C. . . . .	4.835 g. water
„ 10 „ . . . . .	9.330 g. „
„ 20 „ . . . . .	17.118 g. „

From this it can be seen that at 10 deg. C. air saturated with water vapour contains 1.2 per cent. by volume of water vapour. So long as the gas is saturated and the temperature is constant the analysis can be calculated as on a dry-gas basis without error. For instance, if one part by volume of the gas is absorbed in caustic potash, at the same time a corresponding portion of the water vapour is also taken up. The gas remains saturated as before and the percentage of absorbed  $\text{CO}_2$  corresponds to that on the dry gas.

#### Sampling.

The author next describes the methods of sampling, and points out that although sampling tubes of quartz, porcelain, and the like have a number of advantages especially at temperatures above red heat, on cement works sampling tubes made of iron are usually used and have the advantage of mechanical strength. If the temperature of the gas is high a water-cooled tube is required in order to avoid reaction between the gas and the metal. The gas is drawn through tubes of small diameter (5 to 7 mm.) at high velocity.

When iron sampling tubes are used one of the following reactions can occur according to the conditions, e.g. gas composition and temperature.

- (1)  $\text{Fe}_2\text{O}_3 + 3\text{H} = 2\text{Fe} + 3\text{H}_2\text{O}$
- (2)  $2\text{Fe} + 3\text{CO}_2 = \text{Fe}_2\text{O}_3 + 3\text{CO}$
- (3)  $3\text{Fe} + 4\text{CO}_2 = \text{Fe}_3\text{O}_4 + 4\text{CO}$
- (4)  $\text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2$
- (5)  $\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$

Reactions (2) and (3) play an important part in fresh iron tubes. With use a film of  $\text{Fe}_2\text{O}_3$  forms which acts as good protection from further chemical changes. The danger of interaction between the gas and the iron tube is greater with a high temperature and a high water vapour concentration in the gas, with an increase in the area of contact of gas and metal, and with a reduction of the gas velocity along the sampling tube. If the temperature of the gas exceeds 500 deg. C. it will be necessary to use a water-cooled or a quartz tube.

If the gas is drawn by an aspirator 5 to 6 litres of water should be allowed to flow out before a sample is admitted to the Orsat apparatus by a T-tube. Dust is removed by interposing a wad of glass wool in the tube to the apparatus.

The use of petroleum for protecting pyrogallol and cuprous chloride solutions in the Orsat apparatus from the action of the atmosphere may lead to a negative error of as much as 1 per cent. in oxygen and carbon monoxide. A case is quoted where a low value for  $\text{CO}_2$  of 17.2 per cent. was found when the real value was 21.4 per cent. This was traced to the use of an iron tube, and the difficulty was removed by replacing it with a quartz tube.

The author also points out the importance of choosing a suitable position for the sampling pipe. Errors can arise due to the difference in temperature between the gas and the liquids in the Orsat apparatus, and care should be taken that the temperatures are the same. It is important in all cases to clear the tubes from air before the sample is analysed, and several flushings of the tubes with the gas are necessary for this.

---

## Grinding in the Cement Industry.

THE following resumé on present-day trends in grinding in cement factories, by Nathan C. Rockwood, is taken from a recent issue of *Rock Products*.

Two events have made grinding, for the time being at least, the primary consideration of the cement manufacturer. The first was the introduction of the air separator and the general adoption of closed-circuit grinding; the second is the writing of specifications for fineness in terms of specific surface requirements. Air separators have increased the efficiency of all types of mills, when properly used, and will probably be a permanent part of every flow sheet.

Specific surface specifications for fineness may possibly be a passing fad. There is a belief that cement can be ground too finely for practical use, regardless of the apparently well-established theory that no cement particle larger than, say, 25 to 40 microns is ever completely hydrated. Very fine grinding was introduced originally to overcome defects in burning or clinkering practice, and it is possible that with improved burning and clinkering practice it may no longer be needed to ensure sound cements. It may always be necessary for making quick-hardening cements, but even that is not established beyond reasonable doubt; and it may be that quick-hardening cements will not remain popular for every purpose.

### Raw Grinding.

Grinding of raw materials in closed circuit has become almost universal practice. *Fig. 1* shows the ordinary flow-sheet for dry grinding. The sketch shows a Hercules type of mill; this is a pioneer in preliminary grinders, but other types are just as common. A novel arrangement is shown in *Fig. 10*.

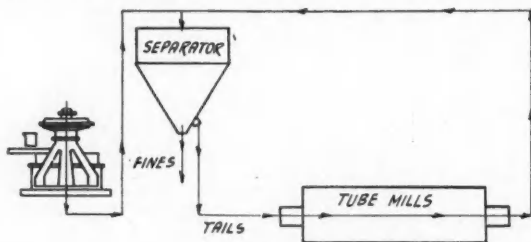


Fig. 1

This is at the Hudson, N.Y., plant of the Universal Atlas Cement Co., where a B. & W. mill is close-circuited with an elevator and air separator. Through this whole system hot air is circulated which dries the raw materials as they are ground and conveyed.

In raw grinding it is taken for granted that there is no purpose in grinding finer than 200-mesh. There are cement makers who are beginning to question this, we believe with good reason; however, it is now the accepted practice. Therefore, the object is to reduce to 200-mesh as quickly and efficiently as possible.

Ball and tube mills are not generally regarded as efficient crushers. Crushing is best done in one or more preliminary crushers or mills, usually in two or three stages. Some say nothing coarser than  $\frac{1}{4}$ -in. material should be fed to a ball mill. It is well known that reducing the size of the material fed greatly increases ball and tube mill capacities.

Dust collectors and air separators make possible the saving of fine material wherever it is made without passing all the material through a tube mill. For this purpose very large circulating loads in preliminary mills are the rule. Here the efficiency of the air separator—its ability to remove 200-mesh material as fast as it is made—is important. While only experience with particular installations and particular raw materials can develop the best combination, the objective is definite and obtainable.

Wet raw grinding is not discussed here, except to note that the tendency is toward closed-circuit grinding using vibrating screens or some other type of slurry separator. It is notable, however, that increasing efficiency of dry grinding, and present possibilities of perfect dry blending, in which the closed-circuit mill-air separator unit is a factor, may reverse the recent trend toward the use of the wet process almost exclusively.

#### **Finish Grinding.**

In clinker grinding the problem is altogether different. No one to-day wants uniformly sized cement, no matter what its particle size. The efficiency of the air separator as such is not so important. Its main function is to keep a large and uniform circulating load going through the tube mill. Instead of holding the material in the mill until it is ground to the required size, it is passed two or more times through the mill. This tends to keep the cement cool, keeps the grinding media cleaner and more effective, and permits selection of more efficient or larger grinding media.

It is not desired to remove all the 200-mesh material as fast as it is made because this would produce a cement without the necessary "flour," and one that would not pass the ordinary specific surface requirements. The mill and air separator unit is not dependent for efficiency on the separator, as in raw grinding, but on a certain specific-surface cement at lowest all around cost.

Since compartment mills introduce additional and unnecessary variables, the tendency is definitely away from compartment mills. The simplest present practice, and the one most likely to yield useful data for control of grinding, is to prepare the clinker in preliminary grinders in one, and often two, stages, such as by the use of small high-speed gyratory crushers, hammer mills, Hercules mills, etc., followed by a preliminary ball mill, and eventually feeding the product to the finish tube mill reduced to at least minus 20-mesh. Each crushing unit may or may not be in a closed circuit, but the tube mill is in a closed circuit. *Fig. 9*, which illustrates the new finish-grinding arrangement at the rebuilt Hudson, N.Y., and Leeds, Ala., plants of the Universal Atlas Cement Co., is a good example of the latest design. *Fig. 2* shows a popular arrangement, of the simplest kind, although other types of preliminary grinders may be used.



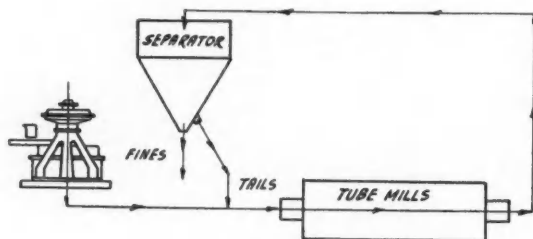


Fig. 2.

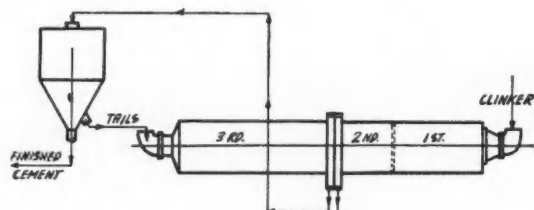
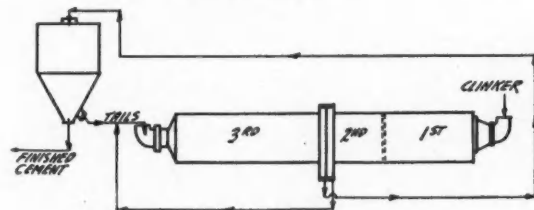
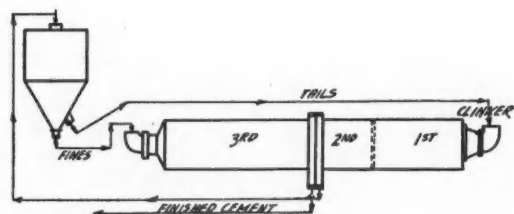


Fig. 3.



Figs. 4 and 5.



Where a preliminary grinder has its own closed circuit with an air separator, as is the case when a B. & W. mill is used as the preliminary grinder, the air separator serves the same function as in raw grinding; it is operated so as to give maximum efficiency as a separator, the object being to skim off the tube mill feed as fast as it is produced, returning the tailings to the preliminary mill. In this case very large circulating loads are employed for best efficiency of the

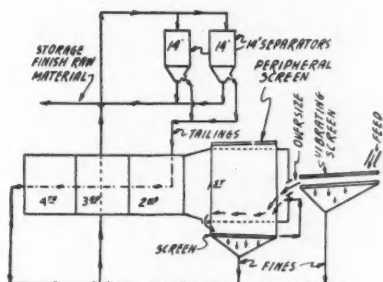


Fig. 6.

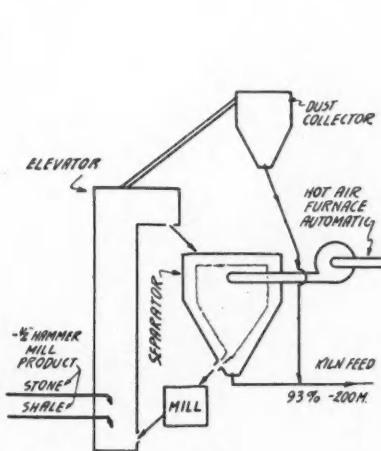


Fig. 7.

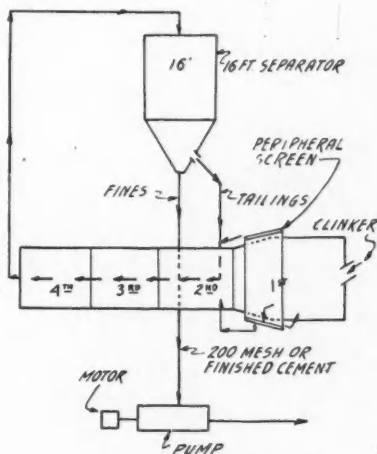


Fig. 8.

entire unit, and, moreover, the effect of fineness of feed in increasing the tube mill capacity must be considered and the entire clinker-grinding installation balanced for efficiency or lowest power and maintenance cost.

Compartment mills of the three- and four-compartment continuous-travel type appear to be definitely losing favour. Figs. 6 and 8 show the latest arrangements using four-compartment mills and air separators for both raw (Fig. 6) and

finish grinding (*Fig. 8*). Air separators were never designed for application to compartment mills. To differentiate the work done in the various compartments and return the tailings of two or more separators to the correct compartment is too much to expect of any plant operator; so many manufacturers are taking out grids and converting compartment mills to simple tube mills.

The big compartment mill seemed the ideal solution to the grinding problem ten years ago. It combined in one unit all the stages of grinding; required no elevators or other handling equipment between stages; required a minimum of space and headroom; and was driven by a single motor. Undoubtedly its compartments and their grinding media could have been adjusted to the particular clinker or raw materials to be ground so as to have served as a very efficient unit. But it had no flexibility in the event of the materials ground not being uniform. It could not grind to 1,100 sq. cm. per gram specific surface and 1,750 sq. cm. per gram specific surface with equal efficiency or facility. Its product when operating most efficiently may have been good cement, but this is not acceptable under many present-day specifications.

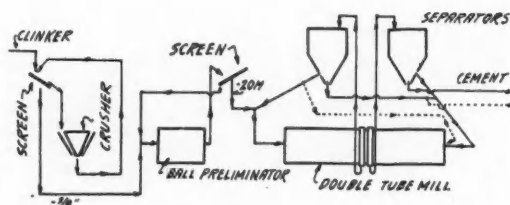


Fig. 9.

The latest substitutes are for the older type of compartment mill shown in *Figs. 3, 4, 5* and *9*. *Fig. 3* illustrates the arrangement at the Allentown Portland Cement Co., and *Fig. 9* the arrangement of the finish grinding units at Hudson and Leeds, which include new type Allis-Chalmers finish mills. In both cases the mills have more than one compartment, but they are fed from both ends and discharge near the middle.

In the case of the Smidth mill at Allentown, the clinker is first crushed and ground (with no preliminary crushing) in the first compartment of the mill. The product of the second compartment goes to the air separator, and the tailings from the separator (the circulating load only) to the third compartment, whose product joins that of the second compartment as feed to the separator. Obviously, there are several possible arrangements. Two of these are shown in *Figs. 4* and *5*. That adopted, at least temporarily, is *Fig. 3*.

#### Summary.

Many refinements may be looked for in grinding practice in the next few years as a result of the knowledge it will now be possible to gain from simple

closed-circuit units where each factor may be studied separately as to its effect on both efficiency and character of product. Moreover, apparatus is being developed that will provide automatic controls for some of these factors.

Factors which must be studied and controlled are (1) the size, amount and uniformity of the material fed; (2) the amount of moisture (in wet grinding)—there is an optimum for grinding efficiency; (3) the speed of the mill—the higher the speed, within limits, the more crushing action of the balls and the greater capacity, also the more power consumed; (4) the size and quantity of the grinding media; (5) the character of the lining; (6) the amount and size of circulating load.

Segregation of the balls or grinding media according to size is desirable; that is the chief function of the grids in compartment mills. It has long been accomplished without grids in conical mills; and it is now being accomplished in tube mills by use of a special type of lining.

---

## Specifications for Building Limes.

THE following note is from the Report of the Building Research Station for the year 1937 :—

Although the method of testing moderately hydraulic limes described in the last Report\* gave satisfactory results at the Station, it did not give sufficiently close results when applied to the same limes in different laboratories.

In consequence it was decided to give up artificial means of accelerating the development of strength of such limes and to rely on simple damp storage for 28 days. Samples of three limes were distributed among four different laboratories and each tested there are four different ages (Table 1). At the Station, in addition, sets of specimens for the 28 days' test were stored at different temperatures to determine the effect of such variation. From these last results it appears that over the range from 16 deg. C. to 20 deg. C. the effect of variation of storage temperature on strength is considerable. The exact temperature of storage was known for only two of the laboratories but those of the other two could be estimated.

The results from each laboratory were consistent amongst themselves; in 35 sets of specimens, six only had coefficients of variation of 10 per cent. or more, of which the highest was 14½ per cent. The agreement between the different laboratories before correction for temperature was not close. When, however, corrections for the different temperatures of storage were made according to the data obtained at the Station it was found that the results from all laboratories were in close agreement.

---

\* "Cement and Lime Manufacture," November, 1937.

The opportunity was taken to compare the results given by eminently hydraulic limes under similar storage conditions. Samples of such limes were therefore obtained from a number of makers who were asked to describe the method of slaking they advised and also to suggest, if possible, an appropriate means of slaking on the laboratory scale. The results so far indicate that the method of slaking is very important and that in inexperienced hands mortars of very low strength may be obtained from limes which are capable of developing high strength.

TABLE I.—HYDRAULIC STRENGTH TEST. MODERATELY HYDRAULIC LIMES

Sample	Laboratories			
	I 6	II 6-12	III 4	IV 4
Number of specimens ..				
<b>A</b>				
Water-lime-ratio (%) ..	66	67	70	70
Strength at days (lb. per sq. in.) with	28 (7.4)	—	—	—
coefficient of variation (%)	59 (4.5)	48 (7.5)	85	—
3 months ..	—	—	84 (6.1)	70 (14.0)
	165 (6.1)	96 (8.3)	143 (10.5)	106 (3.7)
	227 (5.9)	—	195 (5.8)	187 (4.0)
	244 (2.7)	—	—	—
<b>B</b>				
Water-lime-ratio (%) ..	66 low	64.5	68	66
Strength at days (lb. per sq. in.) with	28 (7.4)	32 (2.9)	48 (3.9)	—
coefficient of variation (%)	—	—	50	—
3 months ..	117 (6.9)	66 (7.7)	107	43 (9.1)
	263 (3.5)	—	230 (5.6)	88 (4.4)
	232 (4.1)	—	—	162 (10.4)
<b>C</b>				
Water-lime-ratio (%) ..	66	63	68	—
Strength at days (lb. per sq. in.) with	35 (11.5)	—	72 (9.5)	—
coefficient of variation (%)	79 (8.6)	56 (5.7)	93 (4.2)	—
3 months ..	—	117 (7.4)	146 (6.9)	—
	153 (4.5)	—	245 (14.0)	—
	295 (14.4)	—	—	—
	311 (7.8)	—	—	—

The results also show that there is a more or less continuous gradation of strength between the so-called semi- or moderately-hydraulic limes and those termed eminently hydraulic. What was not so much expected was that the difference is not one of final strength but rather of strength at early ages. Thus a good greystone lime may in damp storage become finally as strong as a good eminently hydraulic lime, but the latter should be considerably higher in strength at 14 and 28 days. If the set of the quick hydrating portions of a greystone lime is retarded by the addition of gypsum, as was done in the past in selenitic limes, so that it is not destroyed during slaking, the difference between the two types is reduced. At the same time it is possible that further work will show that the addition of gypsum is equally beneficial in the case of a number of eminently hydraulic limes.

## Constitution of Cement.

THE work at the Building Research Station on the system  $\text{CaO} - \text{CaO} \cdot \text{TiO}_2 - \text{CaO} \cdot \text{Al}_2\text{O}_3$  has been completed, and is summarised in the Annual Report of the B.R.S. for the year 1937.

In connection with the investigations on the comparative properties of glass and crystalline phases in Portland cement, considerable attention has been paid to microscopic technique. The examination of Portland cement clinker under the microscope can be carried out either with a petrological or a metallurgical microscope. For the former it is necessary either to prepare thin sections which can be viewed by transmitted light or to crush the specimen to a powder and examine by what is usually known as the immersion method. For the metallurgical microscope a polished surface must be prepared and treated by suitable etching reagents, the final specimen being viewed by reflected light. Each method has its advantages, but the examination of thin sections originally led to such real advances in the knowledge of the constitution of Portland cement that it was almost universally adopted as the standard microscopical method so far as Portland cement clinker was concerned. Recently, however, attention has again been turned to the metallographic method and it is now becoming possible to use it as a means for examining parts of the clinker structure which are not shown clearly in thin sections. Briefly it may be said that thin sections are best for examining the silicate minerals, while polished sections promise to be best for examination of the material between the grains.

The work carried out at the Station on this point has essentially been directed to devising a technique for microscopic examination. A method for polishing has been worked out in which the surfaces are previously impregnated with molten sulphur, this substance having been found to be more suitable than resins, in the case of clinkers. For etching the polished specimens a number of reagents has been tried. The final results of these trials are summarised below :

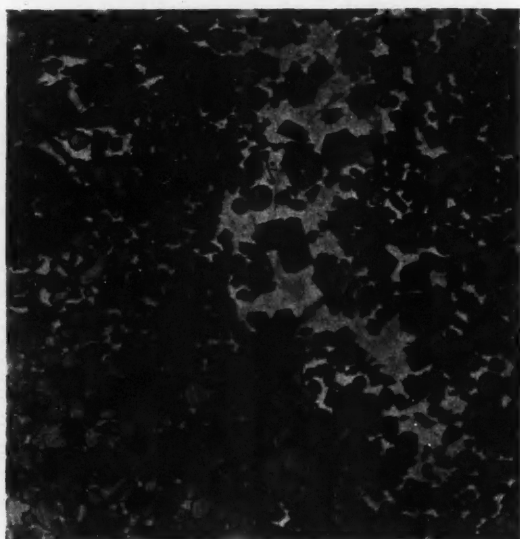
For general work, i.e. to etch the silicate minerals and also to bring up the differentiation of the compounds in the interstitial material, no better reagents have been found than those described by Insley, i.e. preliminary etching in alcohol containing water, followed by etching in a solution of nitric acid in alcohol.

For etching  $3\text{CaO} \cdot \text{SiO}_2$  only, ethylene glycol, etching for a period of three to four hours at room temperatures, or for one hour at 60 deg. C.

For  $2\text{CaO} \cdot \text{SiO}_2$ , exposure to the fumes of concentrated hydrofluoric acid (40 per cent.) for ten seconds. A platinum crucible 2 cm. deep is half filled with the acid and the specimen is placed to rest on the rim of the crucible for ten seconds. This reagent also etches the other compounds, but with the etching period used the  $2\text{CaO} \cdot \text{SiO}_2$  appears darker in colour under the microscope than the other compounds.

For  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ , water alone, etching for twenty seconds.

No etching reagents have yet been found which will etch only the glassy material, and the absolute differentiation of this glassy material from  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$  still depends on experience.



× 400



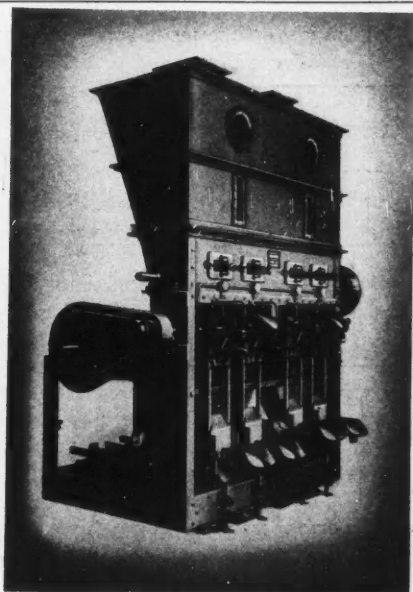
× 500

Fig. 1.—Etched specimens of cement clinker.

The appearance of these polished and etched surfaces is much more clear-cut than that of thin sections, and it is therefore possible to estimate the amount of any constituent, by means of a micrometer stage to the microscope, more accurately than can be achieved with thin sections. In fact with the latter it is rarely possible to do more than estimate the interstitial material as a whole. An analysis of the compound content by this method has been carried out for laboratory-prepared clinkers and also for one commercial clinker. Two photomicrographs of etched specimens are shown in *Fig. 1\**. The upper one ( $\times 400$ ) is a clinker with the interstitial material present entirely as glass. In the lower one ( $\times 500$ ) the interstitial material is completely crystalline and is differentiated by the etching into two constituents,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  and  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ .

An interesting development is the combination of the thin and polished section methods by the production of a thin section with a polished and etched top surface. Although this idea is not new it has been very little used for rock sections and, until its recent introduction by Insley, never previously for cement clinkers. The preparation of the sections is difficult but has been carried out on a few clinkers, mainly of a dense and hard type. The general etching reagent was used and the examination made with a microscope fitted to give either transmitted or reflected light by the turn of a switch. In this way the advantages of both methods are obtained; the main disadvantages are that at present some clinkers

\* Reproduced by permission of H.M. Stationery Office.



### HAVER'S "MODERN" PACKERS

For the automatic filling and weighing of Cement, Lime, Gypsum and other floury materials into

#### VALVE-SACKS

— ★ —

This packer, type 4-BB, fills and accurately weighs 1,200 sacks per hour with ONE OPERATOR.

"Modern" Packers are made with 1, 2, 3 and 4 spouts to handle from 250 to 1,600 sacks per hour.

— ★ —

SOLE BRITISH REPRESENTATIVE:—

**J. DARNLEY TAYLOR**  
17/18, HENRIETTA STREET,  
LONDON W.C.2

TELEPHONE: 9753 TEMPLE BAR

MORE THAN 400 HAVER'S "MODERN" PACKERS IN SUCCESSFUL DAILY USE



do not give good sections, and that, as the exposed top surface is attacked by the atmosphere, the sections are not permanent. The latter difficulty may probably be overcome by the use of cover slip with oil immersion objectives. The method has been used for control purposes in the research on the properties of the glass and crystalline phases in Portland cement.

### Special Cement for Mass Concrete.

THE following is from the "Technical News Bulletin" of the United States National Bureau of Standards:—

The construction during the past ten years of a large number of concrete dams has stimulated a study of the fundamental properties of hydraulic and other cements for use in mass concrete, including the low-heat cement used with success in the Pine Canyon and Boulder dams.

The chief advantage claimed for this cement was its low heat liberation during hydration, as it was expected that this would result in a lower temperature rise within the mass and consequently less contraction during cooling after the concrete had hardened. Thus the number of cracks, which often develop as the mass cools, should be eliminated or greatly reduced.

Later developments have indicated that there are other properties, besides low heat of hydration, which contribute to the success of this cement. To secure further information along this line, Messrs. E. A. Pisapia and F. B. Hornibrook have determined the effect of curing temperature on the modulus of elasticity of concretes made with several types of Portland cements.

Cement.	Modulus of Elasticity ( $E$ ), $10^6$ lb. per sq. in.		Change in ( $E$ ), $10^6$ lb. per sq. in.		Modulus of Rupture at 1 month, lb. per sq. in.	
	40 deg. F.	70 deg. F.	100 deg. F.	40 deg. F. to 70 deg. F.	70 deg. F. to 100 deg. F.	70 deg. F.
High-early strength ..	4.32	4.82	5.11	0.50	0.29	810
Standard Portland ..	4.03	4.36	4.67	0.33	0.31	690
Modified Portland ..	4.10	4.50	4.82	0.40	0.32	740
Portland pozzolana ..	3.45	4.13	4.36	0.68	0.23	610
Low heat .. .. .	2.55	3.31	4.34	0.76	1.03	520

It can be seen from the table that the low-heat cement had a very low modulus at the lowest curing temperature, but the modulus increased rapidly with increase in curing temperature, and at 100 deg. F. was of the same order of magnitude as the modulus of the other cements, except that of the high-early-strength cement.

Although no definite conclusions can be drawn from such limited tests, the data presented indicate that, under conditions of curing found in mass concrete, the modulus of elasticity of the low-heat cements would not be greatly different from the modulus of the standard or "modified" cements.

## Resistance of Cement to Attack by Sea-water and Alkali Salts.

A PAPER by Messrs. T. E. Stanton, jr., and L. C. Meder, describing tests made on the resistance of different cements to the action of sea-water and alkali salts, is published in the Journal of the American Concrete Institute (March-April, 1938). The following conclusions are reached by the authors:

(1) Not all commercial cements are equally resistant to attack by sulphates. Therefore, when structures are subject to more than a normal exposure to sea water and alkali, careful selection should be made in the choice of a cement which will have a relatively high resistance to sulphate attack.

(2) Tri-calcium aluminate is the most injurious compound in cements that are to be used in construction exposed to alkali conditions, therefore, if it is necessary to use cements relatively high in C<sup>3</sup>A content, special care should be exercised in securing a dense well-graded mix including not less than six sacks of cement per cubic yard.

(3) Tetra-calcium aluminoferrite is not a harmful ingredient in cement within the limits covered by the test.

(4) Total aluminates are not as important as C<sup>3</sup>A in determining the potential durability of a cement.

(5) A non-durable standard cement can be modified by the addition of iron ore to the raw mix so that it becomes a highly resistant cement.

(6) A non-durable standard cement can be made more durable by the use of a good siliceous admixture.

(7) Durability is increased by increasing the cement content, provided advantage is taken of the increase in cement to lower the water-cement-ratio and thereby increase the density of the concrete.

(8) Conversely with a given cement content durability can be increased by decreasing the water-cement-ratio if this can be done without sacrificing workability.

(9) If severe weathering conditions are anticipated concrete should contain at least six sacks of cement per cu. yd., a well-graded sound aggregate, and a minimum water-cement-ratio consistent with workability. If the concrete has to be over-worked while being placed, water will segregate and cause an area of comparatively low durability.

(10) There are intangible factors that contribute to the durability or lack of durability of a cement. These factors include the impurities in the raw materials, the manufacturing processes, etc. When more is known about these it will be easier to predict durability from less elaborate tests. At present the calculated compound analysis serves as an indication, but is not sufficient for an accurate relative evaluation of durability, except between cements above and below 8 per cent. in C<sup>3</sup>A content.

(11) It is apparent that increased surface area of the cement due to fine grinding increases durability, but unless it is handled by experienced operators

the use of high-early-strength cement is dangerous due to the possibility of relatively high shrinkage with subsequent cracking. Such cracks form footholds for disintegration.

(12) There is no known accelerated test for durability that can be depended upon in all cases to give accurate information in 28 days. At least six months to a year should ordinarily be allowed under present methods of test.

(13) Dependence should not be placed upon the compound analysis in the relative evaluation of cements until such cements have been thoroughly tested by a proved method for testing durability. After an original comprehensive test, then compound analysis, and possibly the Stenzel or a similar test, can be used for control purposes.

---

## Properties of Asbestos-Cement Sheets.

DURING the past three years the Building Research Board has been carrying out research work on the weathering behaviour of asbestos-cement roofing materials and to determine what tests could suitably be included in a specification. The work has now been completed and is described in the Annual Report of the Board for the year 1937.

The materials examined included flat slates, flat sheets, and corrugated sheets. Accelerated weathering tests have been made on the effects of wetting and drying, freezing and thawing, acid rainwater, and atmospheric carbonation. Only in the case of frost resistance has it been found possible to differentiate in any marked degree between the various products examined. The effects of wetting and drying have been followed by determining at suitable intervals the strength, water absorption, moisture movement, and modulus of elasticity; those of freezing and thawing by visual observation; those of acid rainwater by determinations of the loss in weight; and those of carbonation by measurement of impact strength and other properties.

In wetting and drying tests, 480 cycles of alternate heating at 50 deg. C. and immersion in water at room temperature have been carried out, each cycle normally occupying 24 hours. The changes produced have been in a favourable direction. Moisture movement fell from an initial value of between 0.13 and 0.27 per cent. to between 0.05 and 0.10 per cent. and then remained substantially constant on further exposure. Initial water absorption values varied from 15 to 27 per cent., and after 400 cycles from 6 to 22 per cent. The transverse strength and modulus of elasticity increased during the first 60 to 80 cycles, and subsequently little change occurred. Curves showing the typical behaviour of flat slates in respect of these properties are shown in *Fig. 1*. The reduction in moisture movement, and, to a smaller degree, in absorption, which is found during the life of materials exposed under normal conditions to the weather, is not so large as that obtained in the accelerated weathering tests. One effect which is not favourable to the

product occurs when wetting or drying takes place from one face only of a slate or flat sheet; this tends to cause warping. It seems, however, that this effect is not sufficiently serious to be of much practical importance.

In determining the effect of freezing and thawing, 250 cycles of freezing at  $-15$  deg. C. for 18 hours followed by thawing in water at room temperature for six hours have been carried out. Freezing and thawing eventually cause lamination and flaking, this effect being in general the greater the larger the absorption.

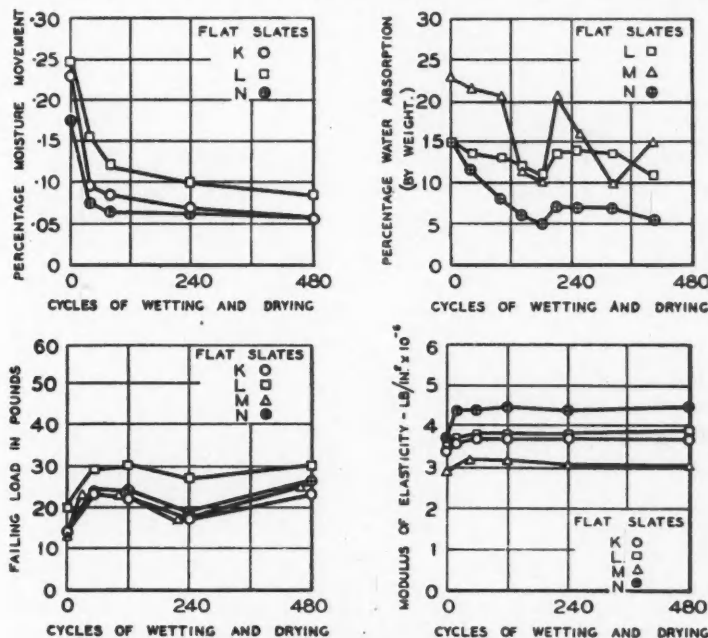


Fig. 1.—Effect of wetting and drying cycles on various properties of asbestos-cement flat slates.

It was also found that the relative resistance of the materials to freezing was related to initial values of the modulus of elasticity. In contrast to the results found for natural stone, the change in elasticity during freezing cycles was not found of any value as a measure of the deterioration produced. Table 1 illustrates the relations found between initial values of absorption and elasticity and the frost resistance.

In order to simulate the solvent action of rainwater, which is acidic owing to the presence of dissolved carbon dioxide or sulphur dioxide, specimens were exposed to running water containing one of these gases in solution. No difference in the rate of attack was found between different materials.

The effect of atmospheric carbonation was determined by measuring the

changes in transverse and impact strength, moisture movement, and shrinkage, of carbonated products. The transverse strength tends to increase as carbonation proceeds, but the impact strength decreases. The moisture movement decreases on carbonation, but at the same time there is an overall shrinkage. This shrinkage is partially offset by the effect of water in producing further hydration of the cement and the reduction in drying shrinkage which accompanies ageing. The net change in length which occurs under exposure to both water and carbon dioxide may amount as a maximum to a shrinkage of about 0.1 per cent. Carbonation of products from one side has been found initially to produce slight warping, but as carbonation proceeds the warping decreases again. The only disadvantageous effects of carbonation are therefore the fall in impact strength and the shrinkage which it produces, the former being the more serious as far as sheeting is concerned. Tests on various types of corrugated sheets exposed on a roof show a fall in impact strength from initial values of 13 to 34 in.-lb. per sq. in. to 10 to 16 in.-lb. per sq. in. after ten years. It seems that this fall in impact strength must be attributed to atmospheric carbonation. This change seems characteristic of the material and, in the case of corrugated sheet roofing, needs to be safeguarded against as far as possible by close spacing of purlins.

The permeability of the material is small and is of the order of  $1 \times 10^{-6}$  c.c. per sq. cm. per second at 24 hours under a pressure head of 20 cm. of water. Tests on materials at ages of one, two and four months show that, in general, transverse strength, water absorption, permeability, and resistance to solution by acid vary little over this period. The moisture movement tends to increase.

The tests proposed for inclusion in a revised specification are transverse strength, water absorption, and a test for resistance to solution by acid waters. The desirability of including a test for permeability has been considered, but its value seems open to question as it appears that when water penetration occurs it happens much more frequently under the lap of tiles than through the material.

TABLE 1.—EFFECT OF FREEZING AND THAWING CYCLES ON ASBESTOS-CEMENT ROOFING MATERIALS, AND RELATION TO MODULUS OF ELASTICITY AND ABSORPTION.

Material	Per cent. water absorption (Wt.)	Modulus of elasticity (lb. per sq. in. $\times 10^{-6}$ )
Flat slates .. .. .	13.5*	3.9*
	14.1	3.6
	16.4	3.2
	22.4	2.9
	24.1	2.7
Flat sheets .. .. .	21.4	2.4
	22.4	2.5
Corrugated sheets .. ..	25.8	2.2

The materials are arranged from top to bottom in decreasing order of frost resistance.

\* These specimens showed no apparent change after 250 cycles of freezing and thawing.

## Formulae for Wet and Dry Grinding.

THE following notes and formulae for measuring the circulating load in wet and dry grinding are given by Mr. F. C. Bond\* in a recent number of *Rock Products*.

When an ore, cement slurry, or any other solid material, is ground wet in closed circuit it is possible to calculate the percentage of the circulating load from the amount of dry feed and water added and the dilutions at various points in the grinding circuit, according to a formula first published in "Mining and Metallurgy," for November, 1937.<sup>(1)</sup>

The circulating load is defined as the ratio of the weight of that portion of the mill product which is returned to the mill feed to the weight of the new feed added to the mill. Both quantities are conveniently expressed in terms of dry tons per hour. The dilution is expressed as parts of liquid to one part of dry solids by weight. It can be obtained from the percentage of solids, or from the specific gravities of the dry solid and the pulp, by the following formula:—

Let  $p$  = percentage of solids by weight,

$s$  = specific gravity of dry ore,

$d$  = specific gravity of pulp.

Then

$$\text{Dilution} = \frac{s - d}{s(d - 1)} = \left(\frac{1}{p}\right)^{-1} \quad \dots \quad (1)$$

The quantities required to calculate the circulating load are:

$F$  = Dry tons per hour of new feed to the mill,

$D$  = Dilution of mill discharge,

$S$  = Dilution of classifier return sand,

$P$  = Dilution of classifier overflow,

$C$  = Tons per hour of new water added to the classifier,

$M$  = Tons per hour of new water added with the mill feed,

$L$  = Dry tons per hour of classifier return sand.

All of these quantities except  $L$  are measured.  $M$  is the sum of  $m_1$  and  $m_2$ , where  $m_1$  is the new water added as liquid to the mill feed, and  $m_2$  is the water contained as moisture in the mill feed. It is evident that

$$PF = C + M \quad \dots \quad (2)$$

and

$$D(F + L) = M + SL \quad \dots \quad (3)$$

It follows that

$$L = \frac{M - DF}{D - S} \quad \dots \quad (4)$$

and

$$L = \frac{PF - C - DF}{D - S} \quad \dots \quad (5)$$

\* Allis-Chalmers Manufacturing Co., Milwaukee, Wis.

(1) Fred C. Bond: "Determination of the Circulating Load in a Wet Closed-Circuit Grinding System," "Mining and Metallurgy," Vol. 18, No. 371, November, 1937.

The percentage of circulating load is  $\frac{100L}{F}$

To calculate the percentage of moisture in the new feed to the mill, equation (2) is solved for  $M$ , and the amount of new water,  $m_1$ , added to the head of the mill is measured in tons per hour.

Then percentage of moisture =  $100 \frac{(M - m_1)}{F}$  .. .. . (6)

If the percentage of moisture in the mill feed is known, the dry tonnage,  $F$ , fed to the mill can be calculated from

$$F = \frac{C + M}{P} \quad \dots \dots \dots (7)$$

In order to obtain periodic determinations of the amount of the circulating load, measurements of the feed tonnage, dilutions, and water added must be made regularly.

The dilution of the classifier overflow is most conveniently measured by weighing samples of the pulp in a bottle of known weight and volume, and calculating the specific gravity of the pulp, from which the dilution is obtained by formula (1). The specific gravity of the dry mill feed can be determined with a pycnometer. For cement slurry it should be about 2.69.

The dilution of the classifier return sands, or oversize, is calculated from the percentage of solids, which is determined by drying a weighed sample. The dilution of the mill discharge can be determined by either of these methods.

The amounts of water added to the classifier and to the mill feed can be measured, either by installing a flow meter in the water lines or by diverting the water for a known interval of time and measuring the amount diverted. Only one of these quantities is necessary for the calculation of the circulating load by equation (4) or (5), but it is preferable to measure both in order to check the result, as well as to check the measured feed tonnage by equation (7).

The following calculation deals with the first-stage grinding of cement slurry in closed circuit with a rake classifier, and will serve as an example:—

Let  $F = 50.00$ ,  
 $D = 0.333$  (75 per cent. solids),  
 $S = 0.177$  (85 per cent. solids),  
 $P = 1.500$  (40 per cent. solids),  
 $C = 8.49$ ,  
 $M = 66.51$ ,  
 $m_1 = 65.01$ .

From equation (4) or (5)  $L$  equals 319.5 dry tons per hour, and the circulating load is 639 per cent. From equation (6) the moisture in the feed is 3 per cent.

In dry grinding in closed circuit with an air separator the circulating load is ordinarily calculated from screen analyses of the mill discharge; return product, or separator oversize; and finished product, or separator undersize. When the percentage passing 200-mesh is determined for these three products the calculation is made by the following formula:—

Let  $g$  = Percentage of minus 200-mesh in mill discharge,



$r$  = Percentage of minus 200-mesh in separator oversize returned,

$u$  = Percentage of minus 200-mesh finished product, or undersize.

Then percentage of circulating load

$$= 100 \left( \frac{u - r}{g - r} \right) \quad \dots \quad (8)$$

Any other convenient mesh size may be used in place of 200, provided that the same mesh size is used for all three products. When the products are sufficiently coarse so that separations can be made at several different mesh sizes, the circulating load calculated from the percentage passing any one mesh can be checked by calculations from the results at other meshes.

It is preferable to use one sieve for all three determinations, since variations between different sieves will cause errors in the result. However, if one sieve is used throughout it may vary considerably from its nominal mesh size without affecting the accuracy of the calculated circulating load.

The following calculation will serve as an example of the method:—

Let  $g$  = 76.4 per cent. passing 200-mesh,

$r$  = 61.4 per cent. passing 200-mesh,

$u$  = 97.5 per cent. passing 200-mesh.

Then from formula (8) the circulating load is 140.7 per cent.

## Recent Patents Relating to Cement and Lime.

### Portland Cement.

482,326. Electric Smelting & Aluminum Co. April 17, 1937.

In treating aluminous siliceous material (felspar, leucite, marl, slag, waste coal products, etc.) to recover alumina, by furnacing a mixture thereof with alkaline earth metal compound (limestone, burnt lime, waste sludges, marl, slag, etc.) and alkali metal compound (carbonates or hydroxides of potassium or sodium, or produced by furnacing aluminous siliceous material with sodium chloride in the presence of steam, etc.) and dissolving out the alkali metal aluminate from the sinter, the residue is treated to form hydrated silica and alkaline earth metal carbonate which are separated. The sinter residue, chiefly di-calcium silicate, is treated with carbon dioxide while suspended in water, forming ortho-silicic acid or other hydrated silica which is filtered off, and calcium bicarbonate. The hydrated silica may contain di-calcium silicate, which will be beneficial as an addition to cement. The bicarbonate in the filtrate is converted by heating

to carbonate which may be used in the manufacture of cement. The active silica itself when added to cement and concrete will counteract the effects of free lime.

### Porous Concrete.

480,681. K. I. A. Eklund. July 25, 1936.

In the production of lightweight stone products by the steam induration of a mixture comprising lime or lime and cement other than slag cement, finely-dispersed siliceous materials such as clay or finely-ground sand, an aggregate if desired, and the minimum of water necessary to form a homogeneous working mixture, the plasticity of the mixture is regulated by the addition of one or more plasticising substances, e.g. sugar, which depress the formation of gels in the mixture and minimise the formation of micropores in the final product.

Examples of plasticising substances are (a) protective colloids, e.g. glue, gelatine, soaps, soluble silicates, emulsions of resinous and fatty acids, spent sulphite and sulphate liquors, (b) peptizers, e.g.

alkali carbonates, amines, (c) buffering substances, e.g. alkali borates or phosphates, ammonium salts, and water soluble salts of organic bases, (d) substances which increase the solubility of lime in water, e.g. sugar, glycerine, ethylene glycol, sulphonic acids, and (e) substances which have an inhibitive action on the hydraulic reaction, e.g. calcium acetate, borax, ammonium carbonate, sodium phosphate, potassium bicarbonate, sodium bicarbonate and acid ammonium phosphate.

When sugar is used as a substance which accelerates the hardening, e.g. calcium chloride, sodium chloride, or water glass, is preferably added to prevent melting during the early stages of the steam induration. The invention is also applicable to mixtures containing cement without lime, except that in this case, when sugar is used as the plasticising agent, it must be accompanied by an accelerator, e.g. calcium or sodium chloride, or by trisodium phosphate or borax as an auxiliary plasticiser. In an example, a mixture of 196 kg. of Portland cement, 40 kg. of lime, 580 kg. of finely-ground sand, 340 kg. of water, 350 gm. of sugar and 1 kg. of trisodium phosphate is made porous by known methods and hardened by steam induration. Other examples are given.

#### Cement Manufacture.

482,831. C. E. Every-Clayton. (N. Ahlmann). October 5, 1936.

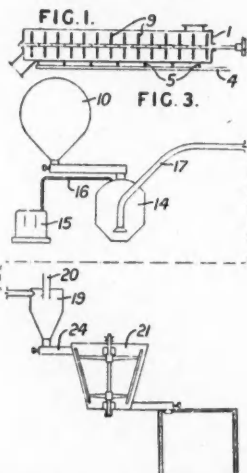
Ready-ground hydraulic cement is treated, during its passage from the grinding mill to a cooler, with air to drive off steam or water vapour. In the apparatus shown in Fig. 1 the ground cement travels along an open-topped trough (1) fitted with rotary stirrers (9) and supplied, through a pipe (4) and nozzles (5), with a small quantity of compressed air. In a modification, the nozzles (5) deliver into chambers covered by porous plates through which the air percolates into the mass of cement in the trough. Fig. 3 shows a further construction in which the cement is delivered from the grinding mill (10) to a chamber (14) supplied through a pipe (16) with air from a compressor (15), the air being admitted after the chamber (14) has been filled and serving to aerate the cement and discharge it through a pipe (17).

### TENDERS WANTED FOR NEW CEMENT PLANT.

— ANCAP —

The Administracion Nacional de Combustibles, Alcohol y Portland, of Montevideo, Uruguay, invites public tenders for the design and supply of installations for Portland Cement Works and Quarry.

Tenders in plain sealed envelopes endorsed "Licitacion No. 556" must state the delivery date and be received by the Gerencia de la ANCAP, Calle 25 de Mayo No. 417, Montevideo, Uruguay, not later than 15 p.m. on the 8th of November, 1938, strictly in accordance with specification and conditions of tender, copies of which may be obtained on application to the European Agents, Duncan, Fox & Co., Ltd., 144, Leadenhall St., London, E.C.3., or directly to the Administracion Nacional de Combustibles, Alcohol y Portland.



The latter delivers to a cyclone separator (19) from which the air escapes at (20) and the cement is conveyed by a worm (24) to a cooling device (21).